Experimental and numerical investigation of flame stabilization and pollutant formation in matrix stabilized ammonia-hydrogen combustion

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\textbf{ABSTRACT}

Ammonia (NH\textsubscript{3}) is a carbon-free fuel that offers an attractive alternative for reducing greenhouse gas emissions. However, the slow flame speed, low heating value, and emissions of nitrogen-containing pollutants present significant issues for practical combustion applications. To address these issues, we investigate the use of matrix stabilized combustion. In this type of burner, combustion is performed within an inert porous ceramic foam, heat is recirculated by solid conduction and radiation, which enhances flame speed and combustion stabilization, thereby permitting combustion over a wide range of equivalence ratios. We present a new porous media burner (PMB) capable of stabilizing NH\textsubscript{3}/air flames at ambient conditions. An extensive experimental characterization of the stability of this burner is conducted with up to 30% by volume of hydrogen (H\textsubscript{2}) in the fuel stream. A 15:1 turndown ratio is demonstrated, with a high thermal power density of 62 MW m\textsuperscript{-3}. Concentrations of NO, unburnt NH\textsubscript{3}, and H\textsubscript{2} in the exhaust stream are measured. Two regimes are identified for low NO operation: rich and very lean. For rich conditions, NO emissions decrease with increasing equivalence ratio and decreasing H\textsubscript{2} blending. Unburnt NH\textsubscript{3} emissions follow opposite trends. These measurements are complemented by simulations in which the burner is represented by a coupled solid-gas reactor network. This model captures the burner’s pollutant emissions to good accuracy and is used to analyze the mechanisms of pollutant formation.

\section{1. Introduction}

The need to reduce anthropogenic emissions of greenhouse gases is driving the rapid transition towards carbon-free fuels [1]. Ammonia (NH\textsubscript{3}), as a storable and energy-dense hydrogen (H\textsubscript{2}) carrier, is an attractive option for applications in energy systems, industrial processes, and transportation [2,3]. After being produced in a low-carbon process, either using conventional methods with carbon capture and storage (“blue NH\textsubscript{3}”), or directly from clean electricity (“green NH\textsubscript{3}”), NH\textsubscript{3} can be inexpensively transported over long distances using an already existing infrastructure, to be used in a number of applications. In the present work, we focus on its use as an energy source for industrial heating, boilers, and electricity production using gas turbines.

An overview of recent research concerned with burner design for NH\textsubscript{3} utilization can be found in Valera-Medina et al. [4], Kobayashi et al. [5], Elbaz et al. [6]. The combustion of NH\textsubscript{3} introduces several challenges, including low laminar flame speeds [7], long ignition delay times [8], low thermal power densities, and high emission levels of several nitrogen-containing pollutants (unburnt NH\textsubscript{3}, N\textsubscript{2}O, NO, NO\textsubscript{2}) [9–11]. It has been shown that blending H\textsubscript{2} with NH\textsubscript{3} can enhance its combustion properties and alleviate some of the issues regarding flame stabilization [7,12]. Swirling injectors have been proposed to stabilize NH\textsubscript{3}/H\textsubscript{2}/air flames over a wide range of operating conditions: from very lean (\(\phi \approx 0.3\)) to rich (\(\phi \approx 1.4\)) equivalence ratios [10,12], with varying levels of H\textsubscript{2} addition [9,10,12,13], over a wide range of operating pressures [9,14], and with steam addition [15]. Several studies have suggested that, for minimal NO emissions, burners should be operated...
at high pressure with equivalence ratios larger than $\phi \gtrsim 1.1$ [4,6]. However, when operating at these fuel-rich conditions, it becomes necessary to adopt a multistage burner design to reduce unburnt NH$_3$ emissions. NO emissions between 10 and 500 ppmv (normalized to 15% O$_2$) have been reported in the literature for high-pressure Rich-Quench-Lean-Combustor with steam addition [9,14]. In contrast, leaner equivalence ratios 0.7 $< \phi < 0.9$ correspond to a maximum in NO emissions for premixed flames, with studies reporting emissions in excess of 4500 ppmv [9,10,12,14,16]. However, very lean conditions ($\phi \lesssim 0.6$) can also result in low NO emissions [10,17–19], although increasing amounts of other pollutants such as N$_2$O and unburnt NH$_3$ may become an issue [11,18,20,21].

One possibility to stabilize flames with low heating value fuels is to use matrix stabilized combustion in porous media burners (PMBs). Over the past three decades, numerous studies have shown that these burners are a suitable technology for the combustion of conventional hydrocarbon fuels in applications such as industrial burners and gas turbines [22–26]. Of particular interest is the suitability of PMBs for NH$_3$ utilization in furnaces and industrial burners, which has not received significant attention [6].

Porous media burners consist of open-cell, highly porous, thermally conductive ceramic foams inside of which combustion is performed. Heat recirculation from the combustion products towards the fresh gas by conduction and radiation within the solid ceramic matrix preheats the unburnt gases, enhances flame speed, and improves flame stabilization, thereby extending the flammability limits to mixtures that are otherwise too lean or too rich for combustion in a conventional burner design [23,25]. In a well-designed burner, excess-enthalpy combustion (also known as super-adiabatic combustion) can be achieved. Specifically, by recirculating heat across the flame, the maximum flame temperature can exceed the adiabatic flame temperature of the reactant mixture. The relationship between super-adiabaticity and flame consumption speed is highly non-linear [7,18], and thus even a moderate increase in excess enthalpy can lead to a significantly higher flame speed and a notable improvement in flame stabilization [25,27,28]. In addition to heat recirculation, flame corrugation and other pore-level effects can further enhance the volumetric fuel consumption rates [29,30]. Experimental and numerical studies of these stabilization mechanisms have been reported, including applications to very lean flames over a wide range of flow rates, fuel compositions, operating pressures, and fuel types [26,31,32]. Recent progress in ceramic additive manufacturing also offers interesting perspectives for the development of novel, application-tailored PMB foam topologies [33–35].

The stabilization of NH$_3$ flames presents similar challenges to that of low-heating-value syngas and very lean hydrocarbon mixtures: a low flame speed with a large flame thickness and a long ignition delay. For very lean conditions and for rich conditions, which have been found to be suitable for low NO operation, these issues are exacerbated [4–6]. Given the non-linear increase of the laminar flame speed of NH$_3$/H$_2$/air flames with preheating [7,18], using heat recirculation and super-adiabatic combustion in a PMB is an attractive concept for overcoming these combustion challenges and stabilizing NH$_3$/H$_2$/air flames. Three experimental studies have presented proof-of-concepts of these benefits: Rocha et al. [36] used an interface stabilized alumina-zirconia PMB with which they characterized the effect of fuel composition on pollutant emissions and ceramic foam temperature distribution. They studied NH$_3$/H$_2$/air and NH$_3$/CH$_4$/air flames operated at $\phi = 0.8$, varying the volume fraction of NH$_3$ in the fuel, and used their experimental measurements to evaluate different chemical mechanisms for NH$_3$ combustion. Nozari et al. [37] performed a more systematic study on NH$_3$/H$_2$/air flame stabilization in a silicon carbide (SiC) PMB at stoichiometric and rich conditions with estimates of combustion efficiency and NO pollutant measurements. Although this study provided a compelling argument in favor of NH$_3$/H$_2$/air combustion inside of SiC PMBs, their results suggest that the flames were not fully stabilized within the porous ceramic foam and instead extended into the exhaust tube. This in turn suggests that the heat recirculation potential of the burner was not fully utilized. In a recent study focusing on lean conditions that had not been extensively considered previously, we demonstrated that a two-zone PMB can stabilize NH$_3$/H$_2$/air flames and that low pollutant emissions can be achieved when the burner is operated near its lean extinction limit [18].

These three studies demonstrate the benefits of matrix stabilized combustion for NH$_3$/H$_2$/air mixtures, but more systematic characterizations of flame stabilization properties and pollutant emissions, in conjunction with computational analysis, are required to optimize these burners and to increase their technology readiness level. Therefore, the present study has four main goals: (1) experimentally examine the stability range of PMBs for varying ranges of NH$_3$/H$_2$/air mixtures, extending previous works by including pure NH$_3$/air flames; (2) provide reference data on flame stabilization and pollutant emission for conditions spanning 70% $< X_{\text{NH}_3} < 100\%$ and 0.6 $< \phi < 1.4$, which extends previous studies to the rich combustion regime; (3) develop and employ reduced-order models to analyze trends in pollutant emissions for NH$_3$/H$_2$/air flames in PMBs; and (4) assess the limitations of such low-order models for predicting premixed NH$_3$/H$_2$/air combustion in PMBs. The experimental and numerical methods used in this study are described in Section 2. The results are then presented in Section 3, specifically focusing on characterizing effects of operating parameters on flame stability and demonstrating, for the first time, that pure NH$_3$ flames can be stabilized in PMBs. We then examine pollutant emissions and use numerical simulations to explain the effect of equivalence ratio on the chemical pathways leading to pollutant formation. Finally, we report our main conclusions in Section 4.

2. Methods

2.1. Experimental setup

The burner is shown schematically in Fig. 1. The porous ceramic matrix is constructed by assembling several cylindrical blocks with a diameter of 50.8 mm: along the streamwise direction, two 25.4 mm-thick blocks of 40 pores per inch (PPI) open-cell yttria-stabilized zirconia-alumina (YZA) foam (Selee, Hendersonville, NC, USA); two 25.4 mm-thick silicon carbide (SiC) foam blocks, the first having a large pore size (3 PPI), the second a slightly smaller one (10 PPI), both manufactured by Ultratex (Pacoima, CA, USA). This is an interface-stabilized burner design, where the flame is stabilized at the boundary between the 40 PPI YZA foam, which is designed to quench the flame, and the 3 PPI SiC foam [38]. In order to minimize heat losses from the outer boundary of the burner, the foams are wrapped in high-temperature ceramic paper (Fiberfrax 550, Unifrax, Tonawanda, NY, USA) and placed within a quartz tube at the bottom of which stainless steel balls are used to homogenize the flow. This assembly is attached to an aluminum base. Compared to our previous design, which consisted of only two foam blocks [18], we have increased the burner’s length for longer residence time, we have thickened the thermal insulation to reduce radial heat losses, and we have increased the pore size of the SiC foam in the main section of the burner to improve flame stability at very lean and rich conditions by increasing the quenching margin. With these modifications, the cell size of the ceramic foam becomes comparable to the large thermal thickness of NH$_3$/air flames [18,38].

Table 1 details the characteristics of these ceramic foams. The geometric properties are determined using a 3D reconstruction
of each foam geometry individually obtained with a Zeiss Xradia Versa 520 X-ray micro-computed tomography (μ-XCT) scanner, operated at an X-ray tube voltage/current of 60 kVp/83 mA for SiC, 140 kVp/71 mA for YZA and a total of 2026 projections to resolve the 3D structure. The 3D reconstructed fields are first smoothed with a 3D Gaussian filter with variance of 2 voxels, and segmented between gas, solid, and internal voxels based on density (thresholding using the adaptive method by Otsu [34,39]) and connectivity. The resolved porosity corresponds to the ratio of gas voxels to total voxels. Pore and cell diameters are estimated using a 3D distance transform watershed algorithm followed by a particle analyzer [40,41].

Experiments are conducted at atmospheric pressure and the reactants are initially at ambient temperature. The flow of all reactants is controlled by an array of mass flow controllers (Alicat, Tucson, AZ, USA, relative accuracy better than 0.8% for present conditions). Chemically pure NH₃ and H₂ (purity better than 99.995%, Linde, Danbury, CT, USA) are used in this study. The uncertainties on equivalence ratios φ and mass fluxes \( \dot{m}_g \) are thus 1.6% and 0.8%, respectively.

### 2.2. Instrumentation and Measurements

Gas analysis is performed immediately upstream of the exhaust of the quartz tube. Gas samples are quenched and dried before measurements. NO and O₂ concentrations are measured using electro-chemical cells (Bridge Analyzers, Bedford Heights, OH, USA). An Emerson Rosemount Analytical thermal conductivity sensor (Shapokee, MN, USA) is used to measure residual H₂ in the exhaust stream when operating at fuel-rich conditions. This instrument has a lower detection limit of 0.5% H₂, which is too high for measurements at lean conditions. Every instrument is calibrated twice daily with standard gases (pure N₂, H₂ in N₂, and NO in Ar from Linde, Danbury, CT, USA) to compensate for drift. NH₃ concentrations are measured using gas measurement tubes from

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**Table 1**

Geometric and thermal characteristics of the porous foams employed in the present work. †: values obtained using X-ray μ-XCT; #: information provided by manufacturer.

<table>
<thead>
<tr>
<th>Description (units)</th>
<th>YZA</th>
<th>SiC</th>
<th>SIC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pore density (PPI)</td>
<td>40</td>
<td>3</td>
<td>10</td>
</tr>
<tr>
<td>Thickness (mm)</td>
<td>2 × 25.4</td>
<td>25.4</td>
<td>25.4</td>
</tr>
<tr>
<td>Porosity ε (%)</td>
<td>82†</td>
<td>84†</td>
<td>84†</td>
</tr>
<tr>
<td>Pore diameter ( d_p ) (mm)</td>
<td>1.11†</td>
<td>1.56†</td>
<td>1.07†</td>
</tr>
<tr>
<td>Cell size ( d_c ) (mm)</td>
<td>2.0†</td>
<td>3.2†</td>
<td>2.6†</td>
</tr>
<tr>
<td>Specific surface ( S_s ) (m⁻¹)</td>
<td>2373*</td>
<td>246*</td>
<td>978*</td>
</tr>
<tr>
<td>Emissivity ε</td>
<td>0.85</td>
<td>0.85</td>
<td>0.85</td>
</tr>
<tr>
<td>Effective density ( \rho_e ) (g cm⁻³)</td>
<td>4.32†</td>
<td>2.62†</td>
<td>2.62†</td>
</tr>
</tbody>
</table>

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**Fig. 1.** (a) Schematic of the experimental apparatus (not to scale). MFC: mass flow controller; SiC: silicon carbide; YZA: yttria-stabilized zirconia alumina; TC: thermocouple. (b) Schematic representation of the reactor network model. \( R_n \) indexes the reactors. The reactor lengths are not to scale, the reader is referred to Section 2.3 for more details.
Gastec (Kanagawa, Japan). All measurements are reported dry and normalized to 15% \( O_2 \) concentration following standard practices for gas turbines [42]:

\[
X_{O_2,\text{dry}} = \frac{X_{O_2,\text{air}} - X_{O_2,\text{ref}}}{X_{O_2,\text{dry}} - X_{O_2,\text{air}}} \times X_{O_2,\text{dry}}, \text{sample}
\]

with \( X_{O_2,\text{air}} = 20.9\% \), \( X_{O_2,\text{ref}} = 15.0\% \) (1)

The manufacturer’s specified measurement uncertainty for the NO, \( NH_3, H_2 \) and \( O_2 \) cells are, respectively, 5%, 10%, 3% and 5%. During our twice daily calibrations, we noted a higher than specified measurement drift for the NO cell and therefore used a larger uncertainty of 11% for these results. All measurements were averaged for at least 2 min after stabilization, leading to a statistical uncertainty better than 4% for the worst case condition reported in the present work. At operating conditions corresponding to extrema in pollutant emissions, measurements were repeated at least 3 times to verify the absence of long term drift. With this, we consider that the relative uncertainties for the normalized NO and \( NH_3 \) emission measurements are 20%, while for unburnt \( H_2 \), which is not normalized, relative measurement uncertainties are estimated to be 7%. In addition to exhaust gas measurements, microtherm-sheathed type-N thermocouples (TC Direct, Hillside, IL, USA) are used to assess flame stability by monitoring exhaust gas and ceramic foam temperatures over time. A NI-9213 thermocouple module within a NI cDAQ-9189 chassis is used to read the measurements. Measurement biases introduced by our thermocouple setup are corrected analytically using the method presented in Appendix A.

The experimental procedure used to determine flame stability is as follows: after reaching a specific operating condition, we wait for thermal stabilization, which is characterized by a maximum change of 10 K over two minutes on all thermocouples installed in the burner; if thermal stabilization can be reached while maintaining combustion within the open-cell ceramic foam, then the operating condition is considered stable. Otherwise, the condition is categorized either as extinction or as flashback, if the flame propagates upstream at \( z \leq 50.8 \) mm.

### 2.3. Reactor network model

To provide further analysis on pollutant formation and to study the effect of heat recirculation within the ceramic matrix, we extend the network model proposed by Mohaddes et al. [25] to include a detailed description of \( NH_3/H_2/air \) chemistry. The low order model consists of \( N_s = 7 \) homogeneous continuously stirred reactors, designated \( R_{\alpha} \), with \( \alpha = 1, \ldots, N_s \), see Fig. 1. The first three reactors \( R_1, R_2, R_3 \) (with respective lengths 38.1 mm, 6.35 mm and 6.35 mm) represent the YZA foam section of the burner, the next three reactors \( R_4, R_5, R_6 \) (lengths 3.12 mm, 3.12 mm and 19.1 mm) represent the 3 PPI SiC foam and the last reactor \( R_7 \) with a length of 25.4 mm represents the 10 PPI SiC. This configuration was found to best reproduce pollutant emissions in the burner with a minimal number of reactors, and adequately models heat recirculation and excess-enthalpy combustion within the burner.

The reactor network is implemented using the extensible reactor network framework of Canteras [43]. The source code for this model is attached as supplementary materials. The gas phase thermo-chemical and transport properties are computed based on the 29 species, 203 reactions mechanism by Stagni et al. [44], which has been validated against experimental measurements conducted at ambient pressure, over a wide range of operating conditions, extending from lean to rich and from hydrogen assisted to pure ammonia [45,46]. A system of \( N_t(2 + N_s) \) ordinary differential equations is solved, where \( N_t \) is the number of species in the chemical mechanism, with two additional equations for the gas- and solid-phase temperatures. Because steady-state combustion is considered, the mass flux is prescribed. Each reactor, indexed with subscript \( \alpha \), is modeled by solving the following governing equations for \( N_s \) species mass fractions \( Y_i \), the gaseous and solid temperatures, \( T_g \) and \( T_s \), respectively:

\[
\rho_{\alpha,g} \frac{dY_i}{dt} = \dot{\omega}_{\alpha,g} + \frac{m_{\alpha}^g A_{CS}}{V_{\alpha,g}} (Y_{i,\alpha-1} - Y_{i,\alpha}), \tag{2a}
\]

\[
\rho_{\alpha,g} \frac{dT_g}{dt} = \frac{m_{\alpha}^g A_{CS}}{V_{\alpha,g}} \left( \frac{\varepsilon_{\alpha}}{\tau_{\alpha}} - \sum_{i=1}^{N_s} h_{i,\alpha-1} Y_{i,\alpha-1} \right) + \dot{q}_{\text{chem,}\alpha} \frac{h_{\alpha,g}(T_{g,\alpha} - T_{s,\alpha})}{\varepsilon_{\alpha}}, \tag{2b}
\]

\[
(1 - \varepsilon_{\alpha}) \rho_{\alpha,s} C_{s,\alpha} \frac{dT_s}{dt} = \dot{q}_{\alpha,g} \left( T_{s,\alpha} - T_{\ell,\alpha} \right) + \dot{q}_{\text{t,loss,}\alpha} = \sigma \varepsilon_{\alpha} (T_{s,\alpha}^4 - T_{\ell,\alpha}^4) \tau \pi D_{\alpha,s} A_{CS} \delta_{\alpha,N_s}. \tag{2c}
\]

where the subscripts \( g \), and \( s \), respectively, designate the gaseous and solid phases, \( \rho_{\alpha,g} \) is the density in reactor \( R_\alpha \) with volume \( V_{\alpha} \) and porosity \( \varepsilon_{\alpha} \); and \( \dot{\omega}_{\alpha,g} \) is the net production rate of species \( i \). \( A_{CS} \) is the cross-sectional area of the burner. For the conservation of energy in the gas phase (Eq. (2b)), \( \dot{c}_{g,\alpha} \) is the isobaric heat capacity of the gas phase, \( \dot{q}_{\text{chem,}\alpha} \) is the heat release rate due to chemical reactions, \( h_s \) is the specific enthalpy, and \( h_{\alpha,g} \) is the volumetric heat transfer coefficient between the solid phase and gas phase. In Eq. (2c), the radiative heat loss \( \dot{q}_{\text{t,loss,}\alpha} \) is given by

\[
\dot{q}_{\text{t,loss,}\alpha} = -\sigma \varepsilon_{\alpha} (T_{s,\alpha}^4 - T_{\ell,\alpha}^4) \tau \pi D_{\alpha,s} A_{CS} \delta_{\alpha,N_s}. \tag{3}
\]

This includes both contributions of radial heat losses on the outer side of the foam and of the end of the burner. \( \sigma \) is the Stefan-Boltzmann constant, \( \tau = 0.5 \) is the estimated optical transmissivity of the insulation layer, \( D \) is the burner diameter, \( L_0 \) is the length of reactor \( R_\alpha \), \( \delta_{\alpha,N_s} \) is the Kronecker delta, and \( T_{\ell,\alpha} = 300 \text{ K} \) is the ambient temperature. Heat transfer between neighboring reactors \( \dot{q}_{\alpha,s,\alpha} \) is modeled by

\[
\dot{q}_{\alpha,s,\alpha} = 2A_{CS} \left( \lambda_{s,\text{eff,}\alpha} + \lambda_{\text{rad}} \right) \left( \frac{T_{s,\alpha-1} - T_{S,\alpha}}{L_{\alpha-1} + L_\alpha} + \frac{T_{s,\alpha+1} - T_{S,\alpha}}{L_{\alpha} + L_{\alpha+1}} \right), \tag{4}
\]

which accounts for both solid heat conduction, and solid radiative heat transfer between neighboring reactors. The effective solid phase heat conductivity, was computed in previous work [26]. The temperature dependency is given by a correlation derived from experimental data by Nilsson et al. [47] and Slack [48]:

\[
\lambda_{s,\text{eff}} = \begin{cases} 0.3 \text{ (Wm}^{-1}\text{K}^{-1}) & \text{for YZA;} \\ 1857(1 - \varepsilon_{\alpha})T_g^{0.5332} \text{ (Wm}^{-1}\text{K}^{-1}) & \text{for SiC;} \end{cases} \tag{5}
\]

with \( T_g \) expressed in K. Similarly, the solid phase heat capacity is given as [49]:

\[
C_s = \begin{cases} 910 - 2.40 \times 10^5 T_g^{-1.15} \text{ (Jkg}^{-1}\text{K}^{-1}) & \text{for YZA;} \\ 1522 - 9.02 \times 10^4 T_g^{-0.82} \text{ (Jkg}^{-1}\text{K}^{-1}) & \text{for SiC;} \end{cases} \tag{6}
\]

The volumetric heat transfer coefficient is computed as:

\[
h_r = \frac{S_r \lambda_{s,\alpha}}{d_h} \tag{7}
\]

using the Nusselt number correlation proposed by Bedoya et al. [29]:

\[
Nu = 3.7Re^{0.38}Pr^{0.25}, \text{ with } Re = \frac{\rho u d h}{\mu g}, \text{ and } Pr = \frac{cp_g \mu g}{\lambda_g}. \tag{8}
\]
with \( u = \dot{m}'' / (\rho_d \epsilon) \) the interstitial gas velocity and \( \mu_d \) the gas phase viscosity. The radiative heat conductivity is computed with the Rosseland model [50]:

\[
\lambda_{\text{rad}} = \frac{16\sigma T_i^3}{3\kappa},
\]

with extinction coefficient \( \kappa = (3/d_p)(1 - \epsilon) \) [51].

### 3. Results

#### 3.1. Flame stabilization

The primary advantage of porous media burners is their ability to enhance the stabilization of flames with poor combustion properties [22–25]. In this section we investigate the stability limits of our PMB as a function of three operating parameters: the mass flux of reactants through the burner \( \dot{m}'' \), the equivalence ratio \( \phi \), and the volumetric ratio of H\(_2\) to NH\(_3\) in the fuel (expressed as the volume fractions \( X_{\text{NH}_3} \) and \( X_{\text{H}_2} \) in the fuel such that \( X_{\text{H}_2} + X_{\text{NH}_3} = 100\% \)). We follow the experimental procedure outlined in Section 2.2 and the results of this systematic investigation are shown in Fig. 2. Regions that have been greyed out in Fig. 2 could not be investigated because of either safety or mass flow controller limitations.

Figure 2 (a) shows that stable combustion can be achieved with pure NH\(_3\) in this burner. This is, to the best of our knowledge, the first demonstration of PMB stabilizing a pure NH\(_3\) flame, and is most likely the result of using a larger pore size and better thermal insulation than in previous studies [18,37]. Stable combustion is achieved for mixture compositions between 0.75 < \( \phi \) < 1.4. This corresponds to the region of sufficiently high laminar burning velocity and sufficiently thin thermal flame thickness to support NH\(_3\)/air flame stabilization [7,18].

Figure 2 (b) shows the stability diagram for the same burner operated with a fuel mixture of \( X_{\text{NH}_3} = 85\% \). At this condition, the maximum mass flux through the burner is increased by 75% compared to the pure NH\(_3\) case and the lean extinction limit decreases to \( \phi_{\text{ext}} \) = 0.65. Increasing the H\(_2\) content further, with \( X_{\text{NH}_3} = 70\% \), yields further improvement of burner stability, with lean extinction limits as low as \( \phi_{\text{ext}} = 0.55 \) being achieved. Figure 2(c) also shows that the burner is able to stabilize flames at mass fluxes of \( \dot{m}'' \) = 1.5 kg m\(^{-2}\) s\(^{-1}\), corresponding to a twofold increase compared to \( X_{\text{NH}_3} = 85\% \). Flashback occurs at low mass flux (0.2 ≤ \( \dot{m}'' \) ≤ 0.3 kg m\(^{-2}\) s\(^{-1}\)), and stoichiometric and slightly rich conditions (0.95 < \( \phi \) < 1.2). At these conditions, the flame is no longer quenched in the YZA foam and slowly propagates upstream. Flashback in porous media and micro-combustion is a complex coupled phenomenon that is currently not well understood. A detailed experimental and theoretical analysis on the flame propagation speed in a meso-scale tubular micro-reactor with heat loss, can be found in Ju and Xu [52]. In this study, the authors found that higher laminar flame speeds lead to higher flame propagation speeds. This explains the occurrence of flashback at 0.95 ≤ \( \phi \) ≤ 1.2 observed in our PMB, as this range of equivalence ratio corresponds to a region of relatively higher laminar speeds for NH\(_3\)/H\(_2\)/air flames [7,18]. However, at low flow rates, Ju and Xu [52] noted the existence of a bifurcation due to the non-linear coupling between the flame and the temperature field of the solid. At a fixed equivalence ratio, the flame propagation speed has a local maximum at a critical flow rate \( \dot{m}_{\text{crit}}'' \) and decreases if the flow rate is reduced below \( \dot{m}_{\text{crit}}'' \). This bifurcation might explain the isolated flashback region observed in Fig. 2(c), where stable combustion is observed at the lowest flow rate \( \dot{m}'' \) = 0.1 kg m\(^{-2}\) s\(^{-1}\).

The turndown ratio of a burner is defined as the ratio between the highest and lowest mass flux at which stable combustion can be achieved. A high turndown ratio is particularly desirable for industrial applications. At \( X_{\text{NH}_3} = 70\% \), we successfully demonstrate a turndown ratio better than 15:1. This is comparable and exceeds state-of-the-art hydrocarbon-fuel-based industrial burners with reported turndown ratios of 1:10 to 1:15 in premixed operation [53]. Note that our NH\(_3\) gas delivery system does not allow to perform experiments at mass fluxes higher than 1.5 kg m\(^{-2}\) s\(^{-1}\) or lower than 0.1 kg m\(^{-2}\) s\(^{-1}\), so that the reported results are a conservative estimate of the potential of NH\(_3\) PMBs for high turndown ratios.

Volumetric thermal power density is defined as the ratio of the thermal power of the combustor to the volume of the combustion region. High power density results in reduced weight, cost, and improved efficiency in many space-constrained devices such as jet engines, gas turbines and furnaces, and is another advantage of porous media combustion. For the purpose of the present work, we compute the power density by considering an ideal combustion efficiency, and we only consider the volume of the combustion region itself in our calculations. For the PMB, we use the volume of the SiC foams independently of whether their entire volume is utilized or not during the combustion process. In this respect the reported volumetric power densities for the PMB are more...
conservative than our estimates for swirl-stabilized flames. Using experimental investigations published in the literature, we estimated the volume of swirl flames based on chemiluminescence images. The highest thermal power density demonstrated in this PMB is 62 MW m\(^{-3}\). This is substantially higher than swirl-stabilized NH\(_3\) flames with comparable exergy, at stoichiometry, and operating under atmospheric pressure. From published experimental studies we estimate that the typical power densities for these swirled NH\(_3\) flames are on the order of 5 to 22 MW m\(^{-3}\) [16,54,55].

3.2. Pollutant emissions

We now focus on pollutant emissions. Table 2 summarizes the operating conditions for which each type of gas analysis measurement has been performed. Figure 3 shows the measured NO and unburnt NH\(_3\) emissions of the PMB, normalized to 15% O\(_2\), when operated at two mass fluxes \(\dot{m}'' = 0.3\) and 0.4 kg m\(^{-2}\) s\(^{-1}\), and three volumetric NH\(_3\) fuel fractions: \(X_{\text{NH}_3} = [70\%, 85\%, 100\%]\). Following a similar trend to swirled NH\(_3\) combustion [4–6,56], high NO production is observed for flames close to stoichiometric conditions, with a maximum reached around \(\phi \approx 0.8–0.9\). A 33% increase in mass flux from 0.3 to \(\dot{m}'' = 0.4\) kg m\(^{-2}\) s\(^{-1}\) yields an increase in NO emissions by 60% when operating at near stoichiometric conditions. Low NO emissions are achieved for rich conditions (\(\phi \geq 1.2\)) and very lean conditions, near the burner’s extinction limit (\(\phi \leq 0.6\)). At lean operating conditions, unburnt NH\(_3\) emissions are generally at or below the lower detection limit of our measurement apparatus. As one approaches the lean extinction limit, unburnt NH\(_3\) emissions quickly increase due to poorer flame stabilization and can reach up to 2% (normalized to 15% O\(_2\)). High unburnt NH\(_3\) emissions are also observed at \(\dot{m}'' = 0.4\) kg m\(^{-2}\) s\(^{-1}\)

<table>
<thead>
<tr>
<th>(X_{\text{NH}_3})</th>
<th>(\dot{m}'') (kg m(^{-2}) s(^{-1}))</th>
<th>(\phi)</th>
<th>Experiments</th>
<th>RNM</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0.3</td>
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<td>yes</td>
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<td></td>
<td></td>
<td>1.1–1.3</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>85</td>
<td>0.3</td>
<td>0.65–1.0</td>
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<td>yes</td>
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<tr>
<td></td>
<td></td>
<td>1.1–1.4</td>
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<td>70</td>
<td>0.3</td>
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<td>0.3</td>
<td>0.45–0.7</td>
<td>yes</td>
<td>yes</td>
</tr>
</tbody>
</table>

Table 2 Summary of operating conditions for which pollutant measurements are performed, and for which numerical simulations with the reactor network model (RNM) are conducted. LDL: measurement are performed but the concentration is below the lower detection limit of the sensor.

Fig. 3. NO and unburnt NH\(_3\) emissions of the burner, measured dry and cold and normalized to 15% O\(_2\) following [42], shown as a function of \(X_{\text{NH}_3}\) and equivalence ratio \(\phi\), for two mass fluxes (a,b) \(\dot{m}'' = 0.3\) kg m\(^{-2}\) s\(^{-1}\) and (c,d) 0.4 kg m\(^{-2}\) s\(^{-1}\). For unburnt NH\(_3\), the colored shaded regions correspond to conditions at which unburnt NH\(_3\) concentrations were below the lower detection limit of the measurement system. Markers and dotted lines are used for experimental data, while continuous lines represent the output of the reactor network model introduced in Section 2.3.
and $X_{\text{NH}_3} = 100\%$, which again can be attributed to poor flame stabilization as these conditions are found near the upper blow-off limit of the burner, see Fig. 2(a). N$_2$O is another significant pollutant associated with NH$_3$ combustion. Although we are not able to report experimental measurements for this pollutant, we discuss these emissions in Fig. S1 of the supplemental materials using our numerical model.

Comparing the results of the reactor network model (continuous lines) with experimental measurements (symbols and dotted lines) in Fig. 3 shows overall good qualitative agreement for NO and NH$_3$ emissions obtained over a wide range of operating conditions. However, the reactor network model is unable to accurately predict lean extinction, blow-off (near $\phi = 0.4$ kg m$^{-2}$ s$^{-1}$ and $X_{\text{NH}_3} = 100\%$) and the increase in unburnt NH$_3$ emission that occurs as one nears the extinction limit. In these operating regions, multidimensional effects such as flame front corrugation, stretch, and local extinction are present, leading to a decrease in combustion efficiency and ceramic foam temperature [30,57,58]. The reactor network model is unable to capture such effects. Nevertheless, good agreement is obtained at stoichiometric and rich operating conditions, which allows to study pollutant formation in these regions using pathway analysis.

The results from the model show that NO is mainly formed in the hot flame region, located near the interface between the YZA and SiC porous ceramic foams, see supplementary materials, Figs. S3 and S4. The magnitude of the formation rate depends on the equivalence ratio and is highest at $\phi = 0.80$. Downstream of the flame region, NO is slowly consumed. At rich conditions ($\phi \geq 1.2$), the formation rate in the flame region and the consumption rate in the post-flame region are of similar orders of magnitude, leading to fairly low NO emissions. On the contrary, at near stoichiometric conditions (0.8 $\leq \phi \leq 1.1$), the consumption rates of NO and NO$_2$ in the post-flame region are up to two orders of magnitude lower than their formation rates in the flame region.

To understand the chemistry of the flame region, associated with high NO formation rates in this burner, we show in Fig. 4 reaction pathway diagrams in this region at two representative equivalence ratios: $\phi = 0.80$ and $\phi = 1.30$. In these diagrams, we follow the elemental fluxes of N. To facilitate a direct comparison between the two cases, all fluxes are normalized by the respective molar fraction of NH$_3$ in the premixed inlet flow containing both fuel and oxidizer. Following N atoms originally present in the fuels and forming NO, one may distinguish three main pathways:

1. direct N$_2$ formation, shown in magenta in Fig. 4;
2. the N$_2$H$_2$ pathway, involving N$_2$H$_2$ and NNH as intermediates, illustrated in blue in Fig. 4;
3. the pollutant pathway, involving NO and N$_2$O as intermediates, illustrated in red in Fig. 4.

The relative weight of each of these pathways is shown for both cases in Fig. 4(c). At $\phi = 0.80$ (Fig. 4(a)), the relative weight of the pollutant pathway (red) is quite high: 72% of N atoms being converted from NH$_3$ to N$_2$ go through this pathway. NO and N$_2$O are thus significant intermediate species in the combustion process of NH$_3$ at this condition. This is in direct contrast with operating at rich conditions (Fig. 4(b)), where we find that the pollutant pathway (red) only accounts for 37% of the N elemental flux in the global reaction NH$_3$ + reactants $\rightarrow$ N$_2$ + products. N$_2$H$_2$ (blue pathway) is mainly formed through the reaction of NH with NH$_2$, so that its formation rate increases at rich conditions. The relative weight of the N$_2$H$_2$ pathway is therefore increased from 8% to 32% when increasing $\phi$ from 0.8 to 1.3, while that of the direct N$_2$ formation remains comparable (20% at $\phi = 0.8$ and 31% at $\phi = 1.3$).

The remainder of the present article will focus on a more detailed analysis of pollutant formation in the two operating regimes found most beneficial for NO emission: rich and very lean combustion. Specifically, we will focus on the effect of secondary
operating parameters ($X_{NH_3}$, burner temperature, and mass flux $\dot{m}'$) on these pollutant emissions.

3.3. Pollutant formation near the lean limit

Operating the porous media burner at conditions near the lean extinction limit is a practical solution for achieving low NO emissions [16–19], and we examine here pollutant formation in this regime. We focus on a single mass flux of $\dot{m}' = 0.3$ kg m$^{-2}$ s$^{-1}$, corresponding to conditions at which very lean operation can be achieved (Fig. 2), and consider $H_2/NH_3$ mixtures with $X_{NH_3} = [55\%, 70\%, 85\%]$. Figure 5 shows the composition of the exhaust gas as a function of equivalence ratio. NO emissions are normalized to 15% $O_2$ to compensate for dilution. At $X_{NH_3} = 85\%$, the extinction limit of the burner is not reached at sufficiently lean conditions to achieve low NO operation: emissions are on the order of 1700 ppmv. Using high $H_2$ blending, at $X_{NH_3} = 70\%$ and 55%, lean extinction limits as low as $\phi = 0.53$ and $\phi = 0.45$, respectively, can be achieved. At these conditions, NO emissions range between 10 and 150 ppmv. In contrast, unburnt $NH_3$, which is generally not a significant issue under lean conditions, is measured at concentrations of 100 to 200 ppmv in the very lean region, and up to 20,000 ppmv at the lean limit. We could not detect unburnt $H_2$ at these conditions, indicating that its concentration is lower than the lower detection limit of 0.5% of our thermal conductivity gas analyzer.

3.4. Pollutant formation in fuel-rich conditions

Figure 6 shows measurements of the volumetric exhaust concentration of NO, unburnt $NH_3$, and unburnt $H_2$, for a constant mass flux of $\dot{m}' = 0.3$ kg m$^{-2}$ s$^{-1}$, as a function of equivalence ratio ($\phi \geq 1.0$) and volumetric fractions of $NH_3$ in the fuel ($X_{NH_3} = [70\%, 85\%, 100\%]$). NO emissions decrease with increasing

![Graphs showing NO, NH3, and H2 concentrations](image-url)

Fig. 5. NO and unburnt $NH_3$ emissions of the burner near the lean extinction limit, measured dry and cold and normalized to 15% $O_2$ following [42]. $\dot{m}' = 0.3$ kg m$^{-2}$ s$^{-1}$. For unburnt $NH_3$, the colored shaded regions correspond to conditions at which unburnt $NH_3$ concentrations were below the lower detection limit of the measurement system.

Fig. 6. Measurements of the NO, $NH_3$, and $H_2$ emissions of the burner operating at rich conditions, measured dry and cold. NO and $NH_3$ are reported normalized to 15% $O_2$ following [42]. The mass flux is kept constant at $\dot{m}' = 0.3$ kg m$^{-2}$ s$^{-1}$. 
equivalence ratio. At $\phi \geq 1.3$, NO emissions are on the order of 50 ppmv. Simultaneously, increasing unburnt fuel concentrations are found in the exhaust gases at richer conditions. A large fraction of these unburnt reactants are in the form of unburnt H$_2$, whose volume fraction in the exhaust gases gradually increases to 12%. For $X_{NH_3} = [70\%, 85\%]$ and $\phi \leq 1.2$, only trace amounts of unburnt NH$_3$ (up to 250 ppmv) are present in the exhaust gases, indicating that almost all NH$_3$ in the fuel stream is either oxidized or reformed. For $X_{NH_3} = 100\%$, significant amounts of unburnt NH$_3$ are present in the exhaust stream at $\phi = 1.2$. This is mainly attributed to the lower flame temperature, which is further discussed in the next paragraph.

In Fig. 7(a), thermocouple measurements for $\phi = 1.1$ show that H$_2$ blending does not significantly impact either the flame anchoring position or the temperature profile. In addition, $\phi = 1.1$, we note from Fig. 6 that the composition of the unburnt reactants in the exhaust is also relatively insensitive to $X_{NH_3}$. In contrast, for $\phi = 1.2$ (Fig. 7(b)), the flame with $X_{NH_3} = 100\%$ has a significantly lower peak temperature than its $X_{NH_3} = 85\%$ and $X_{NH_3} = 70\%$ counterparts. This difference in flame topology and burner operating temperature can be attributed to a lower combustion efficiency with higher unburnt fuel in the exhaust stream (Fig. 6), and to an overall poorer flame stabilization. For $\phi = 1.3$ (Fig. 7(c)) and $\phi = 1.4$ (Fig. 7(d)), more unburnt fuel (NH$_3$ and H$_2$) is found in the exhaust stream. At $\phi = 1.3$ and $X_{NH_3} = 100\%$, the flame is stabilized within the 10 PPI SiC foam ($z \geq 76.2$ mm), with the 3 PPI SiC foam (50.8 $\leq z \leq 76.2$ mm) acting as an extended preheating region. At $\phi = 1.4$ and $X_{NH_3} = 100\%$, the flame is fully blown off. In general, the ratio of unburnt H$_2$ to unburnt NH$_3$ in the burner’s exhaust increases as $X_{NH_3}$ is decreased. Three compounding factors explain this trend: (1) the fuel stream contains less NH$_3$ and more H$_2$; (2) flames tend to stabilize further downstream, thereby decreasing the residence time, and (3) the burner’s operating temperature decreases.

At these rich conditions, we again rely on a reaction pathway analysis with the detailed chemistry reactor network model to analyze our experimental measurements. Similarly to Fig. 4, we focus on the region located around $z = 50.8$ mm, corresponding to the flame location and the region of highest NO formation rate. 1D profiles of temperature, species concentrations, and net formation rate are reported in the supplemental materials, Figs. S5 and S6. We consider the following conditions: $X_{NH_3} = 100\%$ and $X_{NH_3} = 70\%$ for $\phi \geq 0.3$ kg m$^{-2}$ s$^{-1}$ and $\phi = 1.2$, corresponding respectively to one case for which residual NH$_3$ and low NO are present in the exhaust stream and to another case where almost all NH$_3$ is either oxidized or reformed and NO emissions are higher. In Fig. 8(a) and (b), we find similar elemental N pathways between these two cases, and generally a similar structure to that identified in Section 3.2. A significant difference, however, is the rate of NH$_3$ decomposition (NH$_3$ + reactant $\rightarrow$ NH$_2$ + product), which is here a rate limiting step. The reactions associated with this step have an aggregated 20% higher rate for $X_{NH_3} = 70\%$ compared to $X_{NH_3} = 100\%$. These reactions have a high activation energy [44], and therefore a higher sensitivity to the burner’s temperature. The higher gas temperature ($T_x = 2241$ K for $X_{NH_3} = 70\%$, compared to $T_x = 2137$ K for $X_{NH_3} = 100\%$, is therefore the main cause of this decrease in consumption rate. It can be seen that there is a significant difference in the relative weight of the NH$_3$ + reactants $\rightarrow$ N$_2$ + products pathways as a function of $X_{NH_3}$ (Fig. 8(c)): at $X_{NH_3} = 100\%, 46.5\%$ of N$_2$ is formed through the N$_2$H$_2$ pathway (blue arrows), compared to only 21.9% at $X_{NH_3} = 70\%$. On the contrary, the pollutants (NO and N$_2$O) pathway (red arrows) accounts for 47.1% of N$_2$ formation at $X_{NH_3} = 70\%$, but only 30.0% at $X_{NH_3} = 100\%$. A major contributor to this difference in reaction pathways is the higher temperature of the $X_{NH_3} = 70\%$ flame. To conclude this analysis, the lower NO emissions measured experimentally at $X_{NH_3} = 100\%$ can mainly be attributed to two factors: (1) in the flame region, due to a lower gas temperature, the pollutant pathway to N$_2$ formation is less active than for other conditions and 40.0% less NO is created as a reaction intermediate; (2) compounding on this lower NO formation rate, higher concentrations of unburnt NH$_3$, and of NH and NH$_2$ radicals are present in the post-flame region at $X_{NH_3} = 100\%$. This favors the NO rebound pathways, with a 35.4% greater NO consumption rate, thereby further reducing NO emissions.

Mass flux affects heat recirculation, ceramic matrix temperature and flame surface density within the burner. Its effect on burner emissions is therefore both of fundamental and practical interest and is explored in Fig. 9 for $\phi = 1.3$ and $X_{NH_3} = 70\%$. This operating condition is selected because flames can be stabilized over a wide range of mass fluxes, while NO emissions remain relatively low. Higher mass fluxes lead to improved reforming of NH$_3$; the unburnt NH$_3$ emissions in the exhaust decreases while the unburnt H$_2$ volume fraction increases. Extrapolating on the
analysis performed previously, this trend may be explained by higher heat recirculation and operating temperature in the PMB, especially on the downstream side of the burner, in the 10 PPI SiC foam (shown as dark grey in Fig. 10). NO emissions increase rapidly up to $\dot{m}'' = 0.5$ kg m$^{-2}$ s$^{-1}$. This is associated with a rapid increase in the temperature in the 3 PPI foam ($z = 63.5$ mm), which reaches a maximum of 2178 K for $\dot{m}'' = 0.5$ kg m$^{-2}$ s$^{-1}$. Further increasing $\dot{m}''$ yields a small decrease in both the peak temperature measured within the burner and NO emissions.

4. Conclusions

We investigated the matrix stabilized combustion of premixed NH$_3$/H$_2$/air mixtures by combining experiments in a porous media burner and a low-order reactor network model. An interface-stabilized burner design with a large pore size was used in order to avoid quenching of NH$_3$ flames with large thermal thickesses. We demonstrated that this design is suitable to stabilize flames over a wide range of operating conditions, with, for the first time, an
Experimental demonstration that PMBs can be used to stabilize pure NH₃/air flames. We found two additional practical benefits for NH₃ combustion in a PMB:

- a large turndown ratio of at least 15:1, comparable or in excess of state-of-the-art premixed hydrocarbon process burners [53];
- and a high volumetric power density of up to 62 MW m⁻³, approximately three times greater than comparable swirl-stabilized NH₃ flames, which is advantageous for power generation and propulsion applications.

Extensive gas analysis measurements of NO, unburnt NH₃, and H₂ were conducted. A low-order reactor network model was developed, which includes interphase heat transfer and solid phase heat transfer. We found that this model predicted pollutant emissions of this burner to good accuracy, illustrating the importance of capturing heat recirculation and super-adiabaticity. We identified two combustion regimes most favorable for low NO emissions: lean combustion near the burner’s extinction limit ($\phi \leq 0.55$) and rich combustion at $\phi \geq 1.2$. Rich combustion presented a significant difficulty as high levels of unburnt fuel remains in the exhaust stream. However, a large fraction of this unburnt fuel was in the form of H₂. We observed experimentally and confirmed through simulations that the reforming efficiency of the burner, and thus the amount of unburnt NH₃ in the exhaust stream, primarily depended on the burner’s operating temperature. The burner mass flux affected residence time and burner temperature, and we found that this parameter had a second order effect on pollutant emissions: it slightly increased NO emissions but improved the reforming efficiency of NH₃ to H₂. Operation near the lean extinction limit provided NO emissions on the order of 100 ppmv, even though at this condition, high levels of H₂ blending ($\lambda_{NH₃} \leq 70\%$) were necessary to stabilize the flame. Near the lean extinction limit, variable amounts of unburnt NH₃ were present in the exhaust stream. Emissions were generally on the order of 200 ppmv, but reached 20,000 ppmv at one condition. Further research is also necessary to quantify NHₓO emissions, as these may be substantial at very lean conditions.

Although these results show the potential of PMBs as a practical solution for NH₃ fueled furnaces and gas turbines, further work is warranted to tailor porous foams for NH₃ combustion. Leveraging recent progress in ceramic additive manufacturing [33–35], topology gradation might allow to combine regions of large pore sizes required to stabilize NH₃/air flames, with finer pore regions more suitable for heat recirculation. The integration of catalysts onto the porous foam or the addition of exhaust gas post-treatment is another possible pathway for reducing pollutant emissions, and enabling a adoption of porous media combustion technology for NH₃ combustion.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

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Appendix A. Temperature correction procedure for thermocouple measurements

Experimental temperature measurements within porous media burners are a challenging endeavor. In this work, we use 1 mm diameter Nanotherm-sheathed type N thermocouples (TC Direct, Hillside, IL, USA). The relative accuracy of these thermocouples is 0.75%. The NI cDAQ acquisition system introduces an additional measurement uncertainty of ±4 K on the measurement of the thermocouple’s junction temperature. The reported temperatures are averaged over 2 min at a sampling rate of 1 Hz, leading to a statistical uncertainty of 5 K. As a non-platinum based thermocouple was used in the present study, catalytic effects are assumed to be negligible [59].

In our configuration, the main source of measurement uncertainties associated with the use of sheathed thermocouples within porous media burners is therefore the relationship between the temperature at the tip of the thermocouple and the temperatures of the solid and the gas, $T_s$ and $T_g$. It is first useful to assess the level of homogeneity of the temperature field in the radial direction. Thermal losses at the outer cylindrical boundary are the dominant source of radial temperature gradient in the solid. To assess their importance, we use the following Biot number:

$$Bi = \frac{Dq_{loss}}{4(\lambda_{eff,rad} + \lambda_{rad})(T_s - T_{amb})} \quad (A.1)$$

The Biot number increases with the solid temperature $T_s$ and reaches a value of $Bi = 0.1$ at $T_s = 2190$ K in the 10 PPI SiC foam. It is thus reasonable for our purpose to assume a uniform solid and gaseous temperature in the vicinity of the thermocouple. Conductive heat losses through the thermocouple’s sheath, on the other hand, are a well known issue that must be compensated for in our setup [59]. We consider here the case of a cylindrical, 1D, sheathed thermocouple of outer diameter $dTC$ in steady state, inserted in a hot porous foam at a uniform temperature $T_g$, over which a gas at $T_g$ flows. This configuration is represented schematically in Fig. A1. The 1D heat transfer equation for the thermocouple reads:

$$\frac{d^2T}{dx^2} - \frac{4h_c}{dTC\lambda_{TC}}(T - T_g) - \frac{4\sigma e}{dTC\lambda_{TC}}(T^4 - T_s^4) = 0 \quad (A.2)$$

where $T(x)$ is the local temperature of the thermocouple at position $x$, $h_c$ is the conducto-convective heat transfer coefficient between the flowing gas and the cylindrical thermocouple, and $\lambda_{TC}$ is the conductivity of the thermocouple. Following standard fin theory [60], this equation can be recast and linearized using

![Fig A1. Schematic of the model considered for thermocouple correction. The thermocouple is represented by a blue line. In the pink section (thermocouple shown as a dotted line, $-L_{ins} < x < 0$), the thermocouple is surrounded by air at ambient conditions and cooled by natural convection; in the gray section (thermocouple shown as a densely dotted line, $-L_{ins} \leq x < 0$), the thermocouple is within the thermal insulation layer (Ins.) surrounding the porous media and is modeled as adiabatic; in the orange section (thermocouple shown as a continuous line, $0 \leq x \leq L$), the thermocouple is within the porous media and is heated by natural convection from the surrounding gas and by radiation from the hot solid. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)](image-url)
reduced temperatures $\theta_s = T - T_0$ and $\theta_b = T - T_s$, under the assumption $\theta_s \ll \theta_b$, in the ceramic foam:

$$\frac{d^2 T}{dx^2} - \frac{4h_c}{dTC \lambda_TC} \theta_b \frac{d \theta_s}{dTC \lambda_TC} \theta_s = 0, \text{ for } x \geq 0.$$  \hfill (A.3)

The non-dimensional quantity

$$\mathcal{N} = \frac{4 \sigma g \varepsilon T_s^4}{h_c},$$  \hfill (A.4)

a pseudo Nusselt number, thus quantifies the relative weight of radiative and convective heat transfer processes in the overall thermal balance of the thermocouple. $h_c$ is estimated using a Nusselt number correlation for flow over a cylinder $Nu = 0.911 Re^{0.385} P r^{0.333}$ [60], with transport and thermal properties evaluated at the film temperature for a vitiated stoichiometric NH3/air flow [43,44]. Radiative properties for high-nickel alloys from Balat-Pichelin et al. [61] are used. Figure A.2 shows that, in the hot, post-flame region of the burner, $\mathcal{N}$ is on the order of unity, so that radiative and convective heat transfer processes are of similar magnitude. Following results by Zheng et al. [62], who found the temperature difference between solid and gas to be on the order of 10–20 K at steady state in the post flame region of their packed bead burner, we assume local quasi-thermal equilibrium: $\theta_s \approx \theta_b \ll \theta_0$, so that one may tentatively simplify Eq. (A.3) as

$$\frac{d^2 \theta_s}{dx^2} - \frac{\theta_s}{\delta^2} = 0,$$  \hfill (A.5)

where the characteristic thermal length $\delta$ of the thermocouple is

$$\delta = \left[\frac{4}{dTC \lambda_TC} (4 \sigma \varepsilon T_s^3 + h_c)\right]^{-0.5}.$$  \hfill (A.6)

Figure A.3 shows the dependency of $\delta$ to burner operating parameters. If $\delta \ll L$, then heat losses through the thermocouple sheath can be neglected. In the present work, $\delta$ and $L$ are of similar order of magnitude, and Eq. (A.5) must be solved analytically. Because the ceramic foam is moving due to thermal expansion, thermal contact cannot be assured between a thermocouple and the hot ceramic foam. We therefore do not attempt to have contact between the thermocouple and the foam when installing them, and apply a convective/radiative flux boundary condition on the tip of the thermocouple ($x = L$):

$$\frac{d\theta_s}{dx} (x = L) = \left. \frac{dTC}{dTC} \delta \cdot \theta_s (x = L) \right. ,$$  \hfill (A.7)

and use a thermal resistance model at $x = 0$ (see Fig. A.1). The section of the thermocouple located in the thermal insulation layer is considered perfectly insulated, while the thermocouple's tail, located outside the burner, is modeled as an infinitely long cylindrical fin cooled by free convection in a quiescent ambient atmosphere [60]. Equating the heat flux on either side of the thermal insulation layer yields boundary conditions:

$$q(0) = q(-L_{ins}) = \lambda_TC \frac{d\theta_s}{dx} (0),$$  \hfill (A.8a)

$$q(0) = q(-L_{ins}) = \frac{\lambda_TC}{L_{ins}} (T(0) - T(-L_{ins})).$$  \hfill (A.8b)

$$q(0) = q(-L_{ins}) = \left( \frac{4f_c \sigma \varepsilon T_s^3}{dTC} \right)^{0.5} (T(-L_{ins}) - T_{amb}).$$  \hfill (A.8c)

Equations (A.5) – (A.8c) are then solved analytically. Figure A.4 shows the temperature correction $\theta_s$ that must be applied to a measured thermocouple junction temperature. This is calculated for a stoichiometric NH3/air vitiated flow. This analytical correction method, based on a local thermal equilibrium assumption, is used to correct all temperature measurements in the present work. Thermocouples inserted into the YZA foam ($z \leq 50.8 \text{ mm}$) have a typical penetration length of $L \approx 3 \text{ mm}$, while those inserted into
Supplementary material


References


